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POLARIZATION EFFECTS IN TWO-PHONON RAMAN SCATTERING IN CUBIC CRYSTALS

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POLARIZATION EFFECTS IN TWO-PHONON RAMAN SCATTERING IN CUBIC CRYSTALS *

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It is shown how to calculate which irreducible representations are present in any two-phonon state even when the individual phonons are degenerate; and how, using polarization effects, to determine experimentally which Raman active irreducible representations are present in the two-phonon state responsible for any Van Hove singularity in the two-phonon Raman dispersion curve.

I. INTRODUCTION

With the advent of new laser sources, two-phonon Raman scattering will almost certainly become a very widely used tool in the analysis of the phonon spectrum of solids. It is the purpose of this note to point out:
(1) How, with no additional effort beyond the insertion of a polarizer and an analyzer, the experimentalist may determine which of the Raman active irreducible representations (Γ_1^+, Γ_{12}^+, Γ_{25}^+,) are present in the

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two-phonon state responsible for any critical point in the dispersion curve, greatly aiding in the identification of the two-phonon state. (2) If the phonons are degenerate then the critical point consists of a superposition of several Van Hove singularities; if the singularities are of different types, the symmetry content of each one may be determined separately. Thus the quantity of interest (which we calculate for diamond) is the irreducible representations contained in each two-phonon state rather than the sum contained in all the degenerate two-phonon states. The latter was calculated by Birman[1,2] by taking cross products of the one-phonon irreducible representations.

The theory of polarization effects in molecular Raman scattering is well known.[3] For light incident along the y direction and observed along the x direction, depolarization ratios, $\rho = I_y/I_z$, are defined where I_z and I_y are the intensities of the z and y polarizations of scattered light and the incident light is either polarized along the z direction ($\rho \equiv \rho_\ell$) or is completely unpolarized ($\rho \equiv \rho_n$). Birman[2] states that the Raman scattered radiation from cubic crystals is depolarized if $\Gamma_1^+ = 0$ and Γ_{12}^+ or $\Gamma_{25}^+ \neq 0$ as is the case for molecular scattering.[3] This however involves an average over orientations and thus is true only for powdered samples. On the other hand Johnson and London[4] and Burstein[5] discuss ρ_n for one particular orientation of incoming and scattered radiation. We shall demonstrate three cases where $\Gamma_1^+ = \Gamma_{25}^+ = 0$ and $\Gamma_{12}^+ \neq 0$ in which (1) $\rho_\ell = \rho_n = 0$, (2) $\rho_\ell \neq 0$ and $\rho_n \neq 0$ and (3) $\rho_\ell = 0$ and $\rho_n \neq 0$ (in the molecular case $\rho_n = 0 \longleftrightarrow \rho_\ell = 0$). It is therefore our feeling that dipolarization ratios become a somewhat useless concept for crystals.

II. POLARIZATION EFFECTS

The polarization operator responsible for Raman scattering is a second rank tensor and thus may be decomposed into the three symmetrical irreducible representations of the cubic point group

$$\Gamma_1^+ = a_1 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \; ; \quad \Gamma_{12}^{(1)+} = a_{12} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} , \quad \Gamma_{12}^{(2)+} = \frac{a_{12}}{\sqrt{3}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}$$

$$\Gamma_{25}^{(1)+} = a_{25} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} , \quad \Gamma_{25}^{(2)+} = a_{25} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} , \quad \Gamma_{25}^{(3)+} = a_{25} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{1}$$

plus the three fold degenerate anti-symmetric representation Γ_{15}^-. However Loudon[5] has shown the anti-symmetric part of the Raman tensor is usually negligible in one-phonon processes and we shall assume this to be true for two-phonon processes as well. Thus the matrix element between the ground state which has the full cubic symmetry Γ_1^+ and the two-phonon state vanishes unless the two-phonon state contains the Γ_1^+, Γ_{12}^+, or Γ_{25}^+ irreducible representations. Furthermore the polarization of the scattered light is immediately determined by multiplying the polarization vector of the incident light by the tensors Γ_i^α of the representations contained in the two-phonon state to obtain the electric moments $\underset{\sim}{M}_i^\alpha$ induced by the transition. Then using[3]

$$I_i^\alpha = \frac{\omega^4}{2\pi c^3} \left[(\mathcal{I} - \underset{\sim}{k}\underset{\sim}{k}) \cdot \underset{\sim}{M}_i^\alpha \right]^2 \tag{2}$$

where $(\mathcal{I} - \underset{\sim}{k}\underset{\sim}{k})$ projects $\underset{\sim}{M}_i^\alpha$ onto the plane perpendicular to the direction of observation $\underset{\sim}{k}$, we obtain the intensity of the light scattered by the Γ_i^α part of the induced electric moment in the $\underset{\sim}{k}$ direction. Let us assume the radiation to be incident in the [110] direction. We show in Table I the induced electric moments for light polarized in the [001] and [1$\bar{1}$0] directions. Let the scattered radiation be observed in the [1$\bar{1}$0] direction;' then Table II shows the magnitude of the I_i's observed when the analyzer is set to pass [001] and [110] polarized radiation. Thus we see that: (1) with a [1$\bar{1}$0] polarizer and a [110] analyzer we can immediately determine which singularities in the dispersion curve are caused by phonon pairs containing Γ_{12}^+ symmetry, (2) with either a [1$\bar{1}$0] polarizer and a [001] analyzer or a [001] polarizer and a [110] analyzer we determine the Γ_{25}^+ singularities, (3) by subtracting $2/\sqrt{3}$ of the dispersion curve obtained in (1) from the dispersion curve obtained with a [001] polarizer and a [001] analyzer one is left with a dispersion curve whose singularities are due to phonon pairs containing Γ_1^+ symmetry.[7]

Note that for the case displayed in Table II, if $\Gamma_1^+ = \Gamma_{25}^+ = 0$, $\Gamma_{12}^+ \neq 0$ and the incident light is [001] polarized $\rho_\ell = I_{12}(110)/I_{12}(001) = 0$ but if the incident light is unpolarized i. e. contains both [001] and [1$\bar{1}$0] polarizations $\rho_n = I_{12}(110)/I_{12}(001) = \frac{1}{2}\sqrt{3}$. It is also easy to see that if the radiation is incident in the [100] direction and observed along the [010] direction both $\rho_n = 0$ and $\rho_\ell = 0$ but if the radiation is incident along [110] and observed along [001] both $\rho_n \neq 0$ and $\rho_\ell \neq 0$ thus proving that statements about depolarization ratios in crystals are quite meaningless unless both the direction of incidence and observation are specified.

III. SYMMETRY OF TWO-PHONON STATES

According to Phillips[8] there are four types of square root Van Hove[9] singularities (P_0, P_1 or F_1, P_2 or F_2, and P_3) and two types of linear singularities ($P_0(1)$ and $P_3(1)$) leading to discontinuities in the slope of the density of states curve. (These are displayed in Figure 2 of reference 4.) The subscripts specify in how many directions $\omega_1(\underset{\sim}{k}) + \omega_2(-\underset{\sim}{k})$ (the two-phonon energy) is a maximum. The numbers in parenthesis specify in how many directions the derivative of $\omega_1(\underset{\sim}{k}) + \omega_2(-\underset{\sim}{k})$ is discontinuous at the critical point. In Table III we display the Van Hove singularities in the two-phonon density of states at X, L, and W in Ge according to the shell model calculation of Johnson and Cochran[10,4] displayed in Figure 1. The type of singularity depends on the model except for the number of discontinuities in the derivative of $\omega_1(\underset{\sim}{k}) + \omega_2(-\underset{\sim}{k})$ which depends only on crystal symmetry. Therefore only three of the singularities at W can lead to slope discontinuities in the two-phonon Raman dispersion curve.

For each different singularity in Table III we show the calculated Raman active irreducible representations present as well as the infrared active irreducible representation Γ_{15}^{-}. The simplest way to calculate this for non degenerate two-phonon states or to calculate the total contribution from all the degenerate two-phonon states when the singularities at a critical point are all identical (e.g. TO-TO at X or L), is by a method due to Lax and Hopfield.[11, 12] To show how to calculate this in general for individual degenerate two-phonon states we consider particular examples at W and X.

The two Q-lines $(1-\alpha, \alpha, \frac{1}{2})$ and $(1+\alpha, \alpha, \frac{1}{2})$[13] and the Z-line $(1, 0, \frac{1}{2} - \alpha)$ form an orthogonal coordinate system (ξ, η, ζ) at $W = (1, 0, \frac{1}{2})$. Let us consider the degenerate LO-LO, LO-LA, and LA-LA singularities. The degenerate LO and LA phonons transform like

$$\begin{aligned} W_1^{(1)} &= \cos\frac{2\pi}{a}x\, e^{-i\frac{\pi}{a}z} + \cos\frac{2\pi}{a}y\, e^{i\frac{\pi}{a}z} \\ W_1^{(2)} &= \sin\frac{2\pi}{a}x\, e^{-i\frac{\pi}{a}z} + i\sin\frac{2\pi}{a}y\, e^{i\frac{\pi}{a}z} \end{aligned} \qquad (3)$$

If we measure $\underset{\sim}{k}$ from the W point, the degenerate W phonons are mixed by a perturbation of the form $(k_\xi P_\xi + k_\eta P_\eta)$ (analogous to the $\underset{\sim}{k} \cdot \underset{\sim}{p}$ perturbation for electrons). Thus in first order the "$\underset{\sim}{k} \cdot \underset{\sim}{p}$" perturbation splits the degeneracy at W as long as $\underset{\sim}{k}$ is not strictly parallel to the Z-line. (If $\underset{\sim}{k}$ is strictly parallel to Z the degeneracy is not split to any order in "$\underset{\sim}{k} \cdot \underset{\sim}{p}$" as is obvious from Figure 1.) We find the combination of

W functions which diagonalize the "$\underset{\sim}{k} \cdot \underset{\sim}{p}$" matrix are (for $\underset{\sim}{k}$ in any direction)

$$Q_1^{LO} = e^{i\frac{\pi}{4}} W_1^{(1)} + W_1^{(2)}$$
$$Q_2^{LA} = e^{i\frac{\pi}{4}} W_1^{(1)} - W_1^{(2)} \qquad (4)$$

We now create the two-phonon[14] wave functions

$$\text{LO-LO} = (Q_1^{LO})^* \, (Q_1^{LO})$$
$$\text{LA-LA} = (Q_2^{LA})^* \, (Q_2^{LA}) \qquad (5)$$
$$\text{LA-LO} = (Q_2^{LA})^* \, (Q_1^{LO}) \text{ and } (Q_1^{LO})^* \, (Q_2^{LA})$$

By simply operating on these two-phonon functions with the projection operator[15]

$$\mathcal{P}_\alpha^{(i)} = \frac{\ell_j}{h} \sum_R \Gamma^{(i)} (R)_{\alpha\alpha}^* \, P_R \qquad (6)$$

One obtains the basis functions with Γ_i^α symmetry contained in the two-phonon functions. Since we are not interested in a particular Γ_i^α basis function per se but only in whether or not it exists and is different from other Γ_i^α basis functions, it is sufficient to limit the sum over R to operations in the group of the wave vector W. Thus we find (and list in Table III) that the LO-LO $P_o(2)$ singularity and LA-LA $P_2(2)$ singularity both contain $\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$ and that the LO-LA P_2 singularity contains only Γ_{25}^+.

As a further example let us consider again the degenerate LA-LA, LO-LO, LA-LO singularities, this time at X. The degenerate phonons at X transform like

$$X_1^{(1)} = \sin\frac{2\pi}{a}x \qquad\qquad X_1^{(2)} = \cos\frac{2\pi}{a}x \tag{7}$$

The Δ-line $(1-\alpha, 0, 0)$ and the two S-lines $(1, \alpha, \alpha)$ and $(1, -\alpha, \alpha)$ form an orthogonal coordinate system (ξ, η, ζ) at $X = (1, 0, 0)$. The perturbation which mixes $X_1^{(1)}$ and $X_1^{(2)}$ as one goes away from X is of the form $(ik_\xi P_\xi - k_\eta k_\zeta P_{\zeta\xi})$. The combination of X functions which diagonalize this perturbation is

$$\Delta_1 = X_1^{(1)} + e^{-i\varphi} X_1^{(2)} \qquad\qquad \Delta_{2'} = X_1^{(1)} - e^{-i\varphi} X_1^{(2)} \tag{8}$$

where $\varphi = \tan^{-1}(k_\xi P_\xi / k_\eta k_\zeta P_{\eta\zeta})$ and the Δ notation corresponds to the standard notation when $\varphi = \pi/2$. We again create two-phonon wave functions as in Eq. 5 and by operating with the projection operator (6) may determine their symmetry content. However because $X_1^{(1)}$ and $X_1^{(2)}$ are real there is a somewhat easier method to determine the symmetry content of the two-phonon functions. If we divide the set of four functions into two pairs $(\Delta_1)^*(\Delta_1)$, $(\Delta_{2'})^*(\Delta_{2'})$ and $(\Delta_1)^*(\Delta_{2'})$, $(\Delta_{2'})^*(\Delta_1)$ we find that each pair separately forms a complete set of basis functions spanning the space of the group of the wave vector so that each pair with corresponding pairs from the (0, 1, 0) and (0, 0, 1) X points forms a complete set of basis functions for a reducible representation of the full cubic group. The determination of the irreducible representations contained in the reducible representations is straightforward. One finds $\Gamma_1^+, \Gamma_{12}^+$ and Γ_{25}^+ contained in the TA-TA and TO-TO functions and only Γ_{25}^+ contained in the TA-TO functions. When φ takes on the special value zero note that $(\Delta_1)^*(\Delta_{2'}) \equiv (\Delta_{2'})^*(\Delta_1)$. In this case one finds the TA-TO function does not contain even Γ_{25}^+. On the other hand when $\varphi^2 = \pi/2$ note that $(\Delta_1)^*(\Delta_1) \equiv (\Delta_{2'})^*(\Delta_{2'})$. Then one finds that the TA-TA and TO-TO functions do not contain Γ_{25}^+ but still contain Γ_1^+ and Γ_{12}^+. Now to determine the contribution to the Raman scattering from phonons around the critical point one evaluates

$$g_i(E) = \int \delta\left(E - E(k)\right) \mathcal{M}_i(\varphi)\, d^3k \tag{9}$$

where $\underset{\sim}{k}$ is measured from the critical point, $E(\underset{\sim}{k})$ represents the two-phonon energy, and $\mathcal{M}_i(\varphi)$ is a matrix element for the contribution of the i^{th} irreducible representation to the Raman scattering. $\mathcal{M}_i(\varphi)$ is usually taken to be a constant but we have shown here on group theoretical grounds alone that for the TA-TA and TO-TO branches $\mathcal{M}_{25}(\pi/2) = 0$ and for the TA-TO branch $\mathcal{M}_{25}(0) = 0$. Examination of the integral (9) shows $g_{25}(E)$ for the LA-LA branch to still have a linear singularity in spite of $\mathcal{M}_{25}(\pi/2) = 0$. This is because $\varphi = \frac{\pi}{2}$ corresponds to the component of $\nabla_k E$ which is discontinuous and thus never contributed to the singularity. On the other hand $g_{25}(E)$ for the LA-LO branch is no longer a simple square root. However in the limit $E \to E_{cp}$ (where cp means critical point), $g_{25}(E)$ does approach the simple square root obtained when $\mathcal{M}_{25}$ is constant. This is because for $E \to E_{cp}$, $\varphi = \tan^{-1}(k_\xi P_\xi / k_\eta k_\zeta P_{\eta\zeta}) = \pi/2$ over all but a

negligible

part of the volume of integration. Thus we list in Table III that the LO-LO branch (non singular)[16] and the LA-LA branch (linear singularity) contain $\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$ while the LO-LA branch (square root singularity) contains Γ_{25}^+.

This $X_1 - X_1$ critical point is a good example of the advantage to be gained by using polarized light for Raman experiments. With no polarization or with polarizer and analyzer set to pass Γ_{25}^+ scattering, a square root singularity will be seen; the linear singularity will be present but will not be distinguishable in the presence of the square root singularity. With the polarizer and analyzer set to pass Γ_1^+ and/or Γ_{12}^+ but not Γ_{25}^+ scattering, a linear singularity will be seen. This will identify the critical point as the X_1 overtone beyond any doubt.

The author wishes to express his thanks to Professor Eli Burstein for first suggesting to him the possible importance of polarization effects in two-phonon Raman scattering.

TABLE I.

Induced Electric Moments

Incident Polarization	Γ_1	$\Gamma_{12}^{(1)+}$	$\Gamma_{12}^{(2)+}$	$\Gamma_{25}^{(1)+}$	$\Gamma_{25}^{(2)+}$	$\Gamma_{25}^{(3)+}$
[001]	$a_1(001)$	0	$\frac{2a_{12}}{\sqrt{3}}(00\bar{1})$	0	$a_{25}(100)$	$a_{25}(010)$
$[1\bar{1}0]$	$\frac{a_1}{\sqrt{2}}(1\bar{1}0)$	$\frac{a_{12}}{\sqrt{2}}(110)$	$\frac{a_{12}}{\sqrt{6}}(1\bar{1}0)$	$\frac{a_{25}}{\sqrt{2}}(\bar{1}10)$	$\frac{a_{25}}{\sqrt{2}}(001)$	$\frac{a_{25}}{\sqrt{2}}(00\bar{1})$

Electric moments induced by two incident polarizations for each of the symmetric irreducible representations of the polarization tensor.

TABLE II.

Incident Polarization	Scattered Polarization	Non Zero I_i
[001]	[001]	$I_1 = a_1^2 \quad I_{12} = \frac{2a_{12}^2}{\sqrt{3}}$
[001]	[110]	$I_{25} = (2)a_{25}^2$
$[1\bar{1}0]$	[001]	$I_{25} = (2)a_{25}^2$
$[1\bar{1}0]$	[110]	$I_{12} = a_{12}^2$

Non zero I_i's as a function of polarizer and analyzer settings, applicable to [110] incident radiation and a $[1\bar{1}0]$ direction of observation. The factor (2) in I_{25} is present if the $\Gamma_{25}^{(2)+}$ and $\Gamma_{25}^{(3)+}$ induced electric moments are coherent. Note that the factor $\omega^4/2\pi c^3$ in Eq. 3 has been absorbed in the a_i.

TABLE III.

	X		L		W	
TO1 + TO1					$P_1(2)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$
TO2 + TO2	P_o	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$	P_2	$\Gamma_1^+ + \Gamma_{12}^+ + 2\Gamma_{25}^+$	$P_3(2)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$
TO1 + TO2					P_1	Γ_{25}^+
TO1, 2 + LO	$F_1(1)$	$\Gamma_{25}^+ + \Gamma_{15}^-$	P_2	Γ_{15}^-	$P_o(2)$	$\Gamma_{12}^+ + 2\Gamma_{25}^+ + 2\Gamma_{15}^-$
TO1, 2 + LA	$P_3(1)$	$\Gamma_{25}^+ + \Gamma_{15}^-$	P_1	$\Gamma_{12}^+ + \Gamma_{25}^+$	$P_2(2)$	$\Gamma_{12}^+ + 2\Gamma_{25}^+ + 2\Gamma_{15}^-$
TO1, 2 + TA1	P_1	$\Gamma_{12}^+ + \Gamma_{15}^-$	P_1	Γ_{15}^-	$P_1(2)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+ + \Gamma_{15}^-$
TO1, 2 + TA2	F_2	$\Gamma_{12}^+ + \Gamma_{15}^-$			$P_3(2)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+ + \Gamma_{15}^-$
LO + LO	$P_2(1)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$	P_2	$\Gamma_1^+ + \Gamma_{25}^+$	$P_o(2)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$
LA + LA	$P_3(1)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$	P_1	$\Gamma_1^+ + \Gamma_{25}^+$	$P_2(2)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$
LO + LA	P_3	Γ_{25}^+	P_3	Γ_{15}^-	P_2	Γ_{25}^+
LO + TA1	$P_o(1)$	$\Gamma_{25}^+ + \Gamma_{15}^-$	P_o	$\Gamma_{12}^+ + \Gamma_{25}^+$	$P_1(2)$	$\Gamma_{12}^+ + 2\Gamma_{25}^+ + 2\Gamma_{15}^-$
LO + TA2			P_2	$\Gamma_{12}^+ + \Gamma_{25}^+$		
LA + TA1, 2	$F_2(1)$	$\Gamma_{25}^+ + \Gamma_{15}^-$	P_1	Γ_{15}^-	$P_3(2)$	$\Gamma_{12}^+ + 2\Gamma_{25}^+ + 2\Gamma_{15}^-$
TA1 + TA1	P_1	$\Gamma_1^+ + \Gamma_{12}^+ \Gamma_{25}^+$			$P_1(2)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$
TA2 + TA2	F_2	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$	P_1	$\Gamma_1^+ + \Gamma_{12}^+ + 2\Gamma_{25}^+$	$P_3(2)$	$\Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{25}^+$
TA1 + TA2	P_1	0			P_3	Γ_{25}^+

Types of critical points (according to Loudon and Johnson[3]) and Raman and infrared symmetry content of two-phonon wave functions at X, L and W for Ge. The six phonon braches are labled in order of decreasing energy TO1, TO2, LO, LA TA1, TA2 although the phonons have simple longitudinal and transverse polarizations only in certain symmetry directions.

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7. This is true even though the Γ_1^+ and Γ_{12}^+ contributions to I may be coherent i.e. $I = I_1 + 2\ I_1 I_{12} + I_{12}$.

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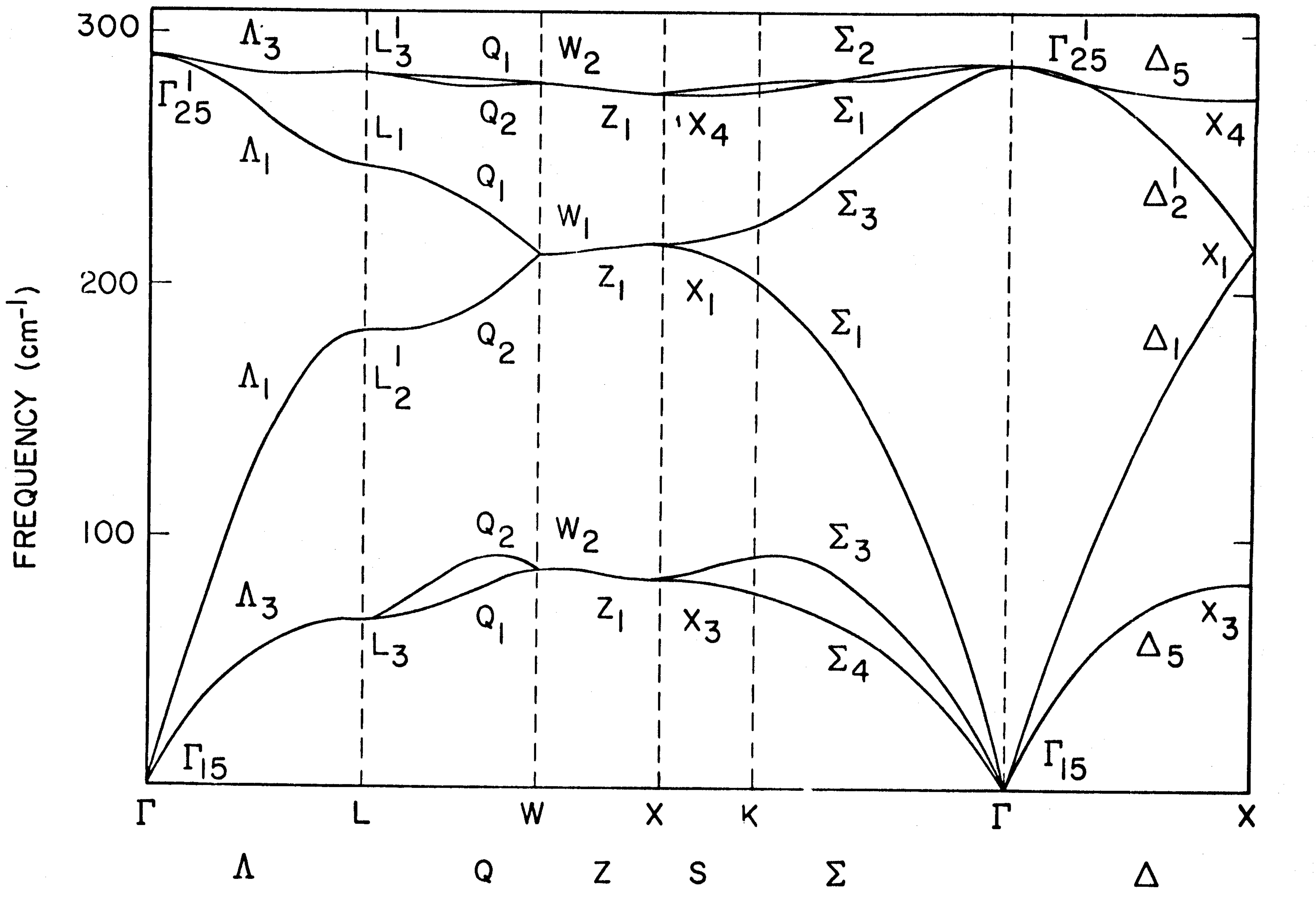
12. LAX, M. Proceedings of the International Conference on the Physics of Semiconductors at Exeter (1962) p. 395.

13. To keep within the usual Brillouin Zone replace $(1+\alpha, \alpha, \frac{1}{2})$ by $(-1+\alpha, \alpha, \frac{1}{2})$ which differs by the (2,0,0) reciprocal lattice vector.

14. To deal with degenerate two-phonon states where the two phonons are not degenerate with each other e.g. LO and LA with TO1 and TO2 is no more difficult. In general more irreducible representations are obtained however because LO-TO1 = $(Q_1^{LO})^*(Q_1^{TO1})$ and $(Q_1^{TO1})^*(Q_1^{LO})$ etc.

15. See for example: M. Tinkham, Group Theory and Quantum Mechanics (McGraw-Hill Book Co., New York 1964) Chapter 3.

16. Actually reference 8 is incorrect (J.C. Phillips agrees) and $P_1(1)$ and $P_2(1)$ points may display linear singularities. However the exact form of the singularity depends on contributions to g(E) from large values of k and hence cannot be predicted from a knowledge of the type of singularity alone.


FREQUENCY (cm⁻¹)
300
200
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Γ
L
W
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Σ
Δ
Γ'_{25}
Λ_3
L'_3
Q_1
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Σ_2
Γ'_{25}
Δ_5
Λ_1
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X_4
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L_3
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Γ_{15}

FIGURE I